

# Electronic thermal conductivity as derived by density functional theory

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(Dated: December 5, 2012)

Reliable evaluation of phonon thermal conductivity is of importance for understanding mechanisms of phonon scatterings and therefore further benefits optimizing figure-of-merit of thermoelectric materials. Usually, when experimentally deriving the phonon mediated thermal conductivity  $\kappa_{ph} = \kappa - \kappa_{el}$  from the measured total thermal conductivity  $\kappa$  the constant Lorenz number  $L_0$  is chosen for estimating  $\kappa_{el}$  according to the Wiedemann-Franz law for simple metals  $\kappa_{el} = TL_0\sigma$ . Present study demonstrates that such a procedure is not reliable when the Seebeck coefficient  $S$  becomes large which is just the case for a thermoelectric material. For a more reliable estimate it is proposed to use the modified Lorenz number  $L_0 - S^2$  which can be directly derived from the measured Seebeck coefficient. Calculations by combining density functional theory with Boltzmann's semi-classical transport theory have been made for the clathrate type-I compound  $\text{Ba}_8\text{Au}_{6-x}\text{Ge}_{40+x}$  with  $x = 0$  and  $x = 0.27$  corresponding to an electron doping of 0.8 states. For  $x = 0.27$  the calculated temperature dependent Seebeck coefficient agrees well with recent experiments corroborating the validity of the density functional theory approach.

PACS numbers: 72.15.Jf, 72.15.Eb, 71.20.-b

Thermal conductivity plays an important role for the thermoelectric performance of a material as expressed by the figure-of-merit  $ZT = TS^2\sigma/(\kappa_{el} + \kappa_{ph})$  which includes the Seebeck coefficient  $S$ , the electrical conductivity  $\sigma$ , and the thermal conductivity  $\kappa = \kappa_{el} + \kappa_{ph}$  summing up the contributions of electronic states and phonon mediated processes. Consequently, a low thermal conductivity in combination with large values of  $S$  and  $\sigma$  are desirable in order to achieve large values of  $ZT$ . Considerable efforts for lowering  $\kappa$  by reducing  $\kappa_{ph}$  were made by utilizing structural properties, such as building up superlattices [1–4] and incorporating suitable filler atom into structural cages [5–12]. These concepts rely on the strong scattering of heat-transporting phonon modes. Often the effect of phonon scattering is taken into account by estimating  $\kappa_{ph}$  with phenomenological formulas. However, neither  $\kappa_{el}$  nor  $\kappa_{ph}$  are directly measured. Rather,  $\kappa_{ph}$  is extracted by subtracting  $\kappa_{el}$  from the measured total thermal conductivity, i.e.,  $\kappa_{ph} \approx \kappa_{exp} - \kappa_{el}$  in which the electronic thermal conductivity is derived by employing the Wiedemann-Franz law for simple metals,  $\kappa_{el} \approx TL_0\sigma$  [6–11, 13–21]. In this expression,  $L_0$  is a universal constant and does not depend on temperature and on the properties of the material under investigation. As will be shown by a density functional theory study for a thermoelectric materials this assumption of a simple metal may lead to unreliable estimates in particular when the Seebeck coefficient of the material is large.

The present theoretical study of the electronic thermal conductivity is based on the same density functional theory (DFT) concept as used for first-principles calculations of Seebeck coefficients (for example, see Ref. [22]). The Wiedemann-Franz law is generalized by introducing a material and temperature dependent Lorenz tensor  $\mathbf{L}$ .

For its calculation Boltzmann's transport theory is applied in combination with electronic properties as derived by a DFT calculation. This procedure is applied for the clathrate type-I compound  $\text{Ba}_8\text{Au}_{6-x}\text{Ge}_{40+x}$ , which is a prototypical thermoelectric material and for which also recent measurements of Seebeck coefficients are available.

The Wiedemann-Franz law is generalized to

$$\kappa_{el} = T\mathbf{L}\sigma, \quad (1)$$

in which the tensor  $\kappa_{el}$  is related to the conductivity tensor  $\sigma$  of Eq. A.2 via the Lorenz tensor  $\mathbf{L}$ . These quantities as well as the Seebeck tensor  $\mathbf{S}$  (Eq. A.3) are second rank tensors [23]. In accordance with Boltzmann's transport theory one derives [24]

$$\kappa_{el} = \frac{1}{T} (\mathbf{K}_2 - \mathbf{K}_1^2 \mathbf{K}_0^{-1}). \quad (2)$$

for which Eq. A.2 is utilized for the definition of the tensor  $K_n$ . The Lorenz tensor  $\mathbf{L}$  can now be formulated as

$$\mathbf{L} = \mathbf{L}_1 - \mathbf{S}^2 \quad (3)$$

whereby  $\mathbf{L}_1$  is expressed as [24]

$$\mathbf{L}_1 = \frac{1}{e^2 T^2} \mathbf{K}_2 \mathbf{K}_0^{-1}. \quad (4)$$

For a free-electron like metal the the second term at the right hand side of Eq. 3 is negligible. In this case the Lorenz tensor can be approximated by  $\mathbf{L} \approx \mathbf{L}_1$ . Inspecting Eq. 3 it becomes obvious that the deviation from the free-electron like behavior is given by  $-\mathbf{S}^2$ . At low temperatures for a simple metal the original Wiedemann-Franz law is a reasonable approximation, i.e.  $\mathbf{L}_1 \approx \mathbf{L}_0$ ,

whereby  $\mathbf{L}_0$  would be a tensor with constant coefficients  $L_0 = \frac{\pi^2 k_B^2}{3} = 2.44 \times 10^{-8} W\Omega/K^2$ .

When assuming the constant relaxation time approximation –as it is also standard for first-principles calculations of the Seebeck coefficients [22]–  $\tau$  cancels out in the components of  $\mathbf{L}$  since it appears in the numerator and denominator according to Eqs.3 and 4. This is also the case for the Seebeck coefficients given by Eq. A.3. For the following discussion it should be noted that crystal structure of the material under study is of cubic symmetry. As a consequence of this high symmetry all the second rank tensors as mentioned above are diagonal and the three diagonal coefficients are equal. Therefore, only one coefficients needs to be considered for each tensor. However, the derivations and calculations can be done for a general crystal symmetry and for tensors with less symmetry and more components. If the tensors are symmetry averaged again only one coefficients needs to be considered.

What remains for the calculation of the integrals appearing in Eq. A.2 is the calculation of the electronic structure and related properties of the actual solid material, which was done for  $\text{Ba}_8\text{Au}_6\text{Ge}_{40}$  by DFT. For that, the Vienna *Ab initio* Simulation Package (VASP) [25, 26] was used for which the pseudopotentials were constructed according to the projector augmented wave method [27, 28]. The exchange-correlation functional was parametrized in terms of the local density approximation according to Ceperley and Alder [29]. The valence state configuration for the construction of the pseudopotentials included the 5s, 5p and 6s states for Ba, the 6s and 5d states for Au, and the 3d, 4s and 4p states for Ge. For the Brillouin zone integration a  $5 \times 5 \times 5$  grid of  $\mathbf{k}$ -points was chosen, which results in well-converged total energies and fully relaxed structural parameters as given in the caption of Fig. 1(a). Electronic transport properties were derived by solving the semi-classical Boltzmann transport equation within the constant relaxation time approximation as implemented in the program package BoltzTrap [22, 30, 31]. For that purpose the Kohn-Sham eigenvalues  $\varepsilon_i(\mathbf{k})$  were determined on a very dense  $25 \times 25 \times 25$  grid of  $\mathbf{k}$ -points.

Fig. 1(a) shows the density of states (DOS) around Fermi energy. A gap of about 0.3 eV occurs about 0.15 eV above the Fermi energy  $E_F$  for the undoped case. The electron doping of  $\Delta N = 0.8$  places  $E_F$  very close to the gap where the DOS changes rather strongly. For such a situation one would expect a large Seebeck coefficient, as is indeed the case (see inset in Fig. 2). By adding  $\Delta N = 2$  electrons the corresponding  $E_F$  falls into the gap. For  $T=300\text{K}$  Fig.1(b) depicts the coefficients  $L$  and  $L_1$  of the cubic Lorenz tensors according to Eqs. 3 and 4) as functions of the doping. It is obvious that the deviation between the approximation  $L_1$  and  $L$  of the full calculation increases strongly the closer the doping is to  $\Delta N = 2$ . It should be noted that for  $\Delta N = 2$  the coefficients  $L$  and  $L_1$  are undefined because no electronic states are available for transport and, subsequently, the

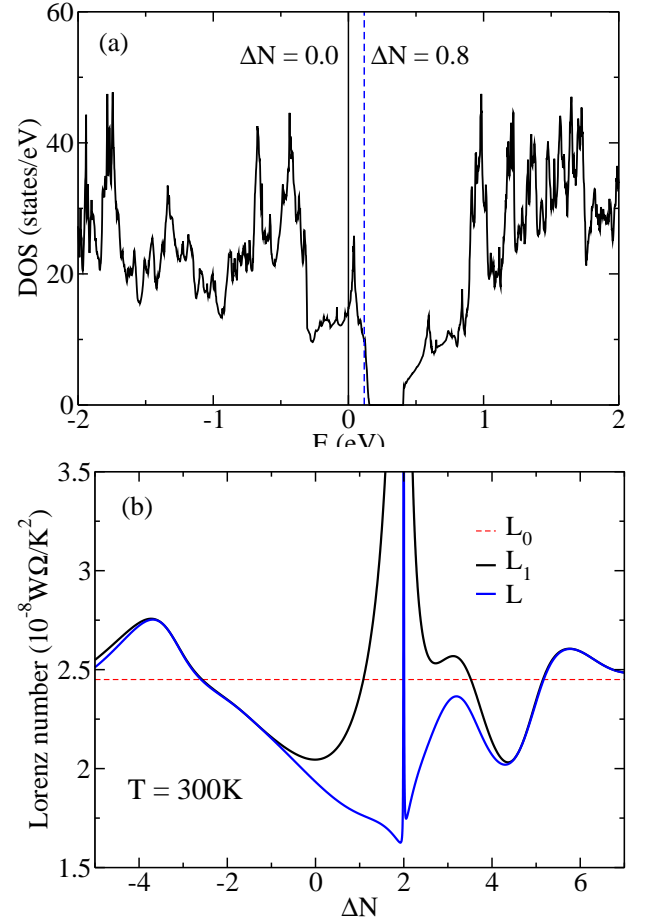


FIG. 1. DFT results for  $\text{Ba}_8\text{Au}_6\text{Ge}_{40}$ : (a) density of states (DOS) vs. energy  $E$  whereby the Fermi energy for the undoped case corresponds to  $E = 0$ . The Fermi levels for the undoped ( $\Delta N = 0.0$ ) and an electron doped ( $\Delta N = 0.8$  or  $x = 0.8/3$ ) compound are indicated by a full and dashed line, respectively. Doping was modelled by the rigid band approximation, i.e. by a suitable shift of the Fermi energy with respect to the undoped case but leaving the DOS unchanged otherwise.  $\text{Ba}_8\text{Au}_6\text{Ge}_{40}$  has the type-I clathrate structure (cubic unit cell, space group  $Pm\bar{3}n$ ). The relaxed structural parameters are 10.70 Å for the cubic lattice parameter and the site specific coordinates are  $2a$  (0,0,0) and  $6c$  (0.25,0.5,0) for Ba,  $6d$  (0.25,0.5,0) for Cu,  $16i$  (0.183, 0.183, 0.183) and  $24k$  (0, 0.117, 0.309) for Ge. (b) Coefficient  $L$  of the cubic Lorenz tensor and its approximation  $L_1$  (Eqs. 3, 4) at 300K vs. rigid-band doping  $\Delta N$ . Negative(positive) values correspond to hole(electron) doping. For  $\Delta N = 2$  the Fermi energy falls into the gap of the DOS. The constant Lorenz number  $L_0$  of the Wiedemann-Franz law is indicated by a dashed horizontal line.

electrical conductivity  $\sigma$  is zero at lower temperatures. The comparison between  $L_1$  and  $L$  demonstrates the effect of the contribution of the Seebeck coefficient,  $-S^2$ . Significant deviations occur in the range of  $0 \leq \Delta N \leq 4$ . For dopings outside this critical region the coefficients  $L$  and  $L_1$  coincide and their values are comparable to the constant Lorenz number but still  $L_0$  might be off by

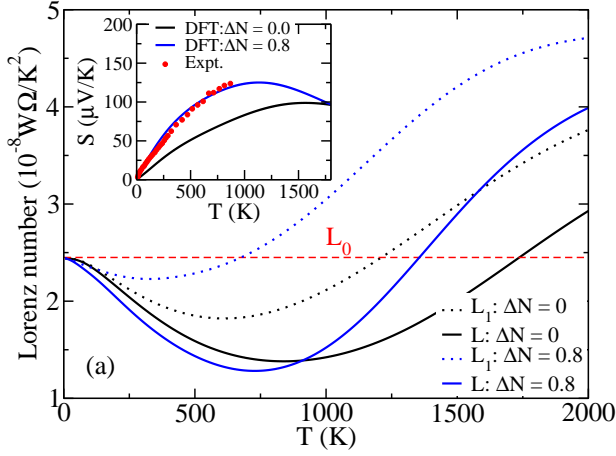


FIG. 2. DFT results for  $\text{Ba}_8\text{Au}_{6-x}\text{Ge}_{40+x}$ : Coefficient of the Lorenz tensor as a function of temperature for no doping (black solid line) and for a doping of  $\Delta N = 0.8$  electrons (blue dashed line), see Fig. 1. The constant Lorenz number  $L_0$  of the Wiedemann-Franz law is indicated by a dashed horizontal line. The inset shows the corresponding DFT-derived Seebeck coefficients in comparison to the experimental values of Ref. [32].

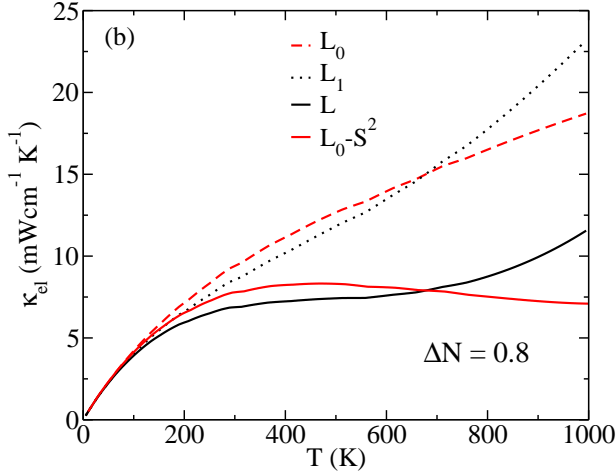


FIG. 3. DFT results for  $\text{Ba}_8\text{Au}_{6-x}\text{Ge}_{40+x}$  with a doping of  $\Delta N = 0.8$  electrons: electronic thermal conductivities  $\kappa_{el}$  as calculated by using the coefficient  $L$  of the full Lorenz tensor, the coefficient  $L_1$  of its free-electron approximation, the constant coefficient  $L_0$  and the suggested approximation  $L_0 - S^2$ .

20%. When the Fermi level is sufficiently far away from the gap,  $L$  has almost the same value as  $L_1$ . The results suggest that the approximation of Eq.(4) is not valid for thermoelectric materials with large Seebeck coefficients and it will lead to an overestimation which might be large.

Fig. 2 shows the temperature dependent coefficients  $L_1$  and  $L$  for no doping and  $\Delta N = 0.8$ . The inset compares DFT derived and experimental Seebeck coefficients revealing rather good agreement between calculation and measurement for the DFT data corresponding

to  $\Delta N = 0.8$ . This change in valence electron number refers to the slightly off-stoichiometric composition  $\text{Ba}_8\text{Au}_{6-x}\text{Ge}_{40+x}$  with  $x = 0.8/3$ , which is within the error bar of the measured stoichiometry [32]. Both  $L_1$  and  $L$  approach the Wiedemann-Franz limit  $L_0$  at low temperatures but deviate significantly at elevated temperatures. Overall,  $L$  and  $L_1$  exhibit a strong temperature dependency and the deviation of the constant value  $L_0$  gets large in particular around 700K, which is in the range of temperatures as they occur in technological applications.

For finally deriving the electronic thermal conductivity  $\kappa_{el}$  from Eq. 1 the full Lorenz coefficient  $L$  together with its approximations  $L_1$  and  $L_0$  is used. The results of in Fig. 3 reflect the behavior of the Lorenz coefficients in Fig. 2 showing again very significant differences up to 40% between the full calculation and the result involving the approximations  $L_1$  and  $L_0$ . Clearly, just using the classical Wiedemann-Franz law (i.e.  $L_0$ ) may lead to rather unreliable values for the electronic thermal conductivity. If then  $\kappa_{el}$  is used for deriving the lattice thermal conductivity from  $\kappa = \kappa_{el} + \kappa_{ph}$  the results for  $\kappa_{ph}$  will also be unreliable. Comparing the rather similar behavior of  $\kappa_{el}$  in Fig. 3 as calculated with  $L_1$  and  $L_0$  it seems a suggestive strategy to correct the Lorenz constant  $L_0$  by subtracting  $S^2$  as is done in case of  $L_1$  in Eq. 3. Doing this gives good agreement with results as derived from the coefficient  $L$  of the full Lorenz tensor, as shown in Fig. 3. Therefore, if the temperature dependent Seebeck coefficient  $S(T)$  of a material is measured in combination with the electric conductivity by applying the corrected Lorenz number  $L_0 - S^2$  a more reasonable estimate is achieved for the electronic thermal conductivity and, consequently, for the lattice thermal conductivity than it is the case when only  $L_0$  is used. Achieving reasonable estimates for  $\kappa_{ph}$  by reasonable estimates of  $\kappa_{el}$  is of importance for optimizing transport properties of thermoelectric materials.

In summary, in this work separating the electrical and lattice thermal conductivities, i.e.,  $\kappa_{el}$  and  $\kappa_{ph}$ , using Lorenz number is studied. Calculations were performed by hybridizing DFT and Boltzmann transport theory, which shows that the Lorenz number in general is a material and temperature dependent quantity rather than a constant value as it is usually derived from the metallic limit. In particular, significant deviations from the constant value are yielded when compound is a good thermoelectric material. Using the constant Lorenz number causes severe discrepancies in the resultant  $\kappa_{el}$  from that using fully calculated Lorenz number, which become significant at higher temperatures. In the present study, an error about 40% at 1000 K was obtained for  $\text{Ba}_8\text{Au}_6\text{Ge}_{40}$ . The results suggest that one has to rethink the way of extracting  $\kappa_{el}$  and  $\kappa_{ph}$  from experiment in the usual way. To remedy this situation, we propose that instead simply using the constant Lorenz number for all materials over all temperatures, one needs to subtract the square of Seebeck coefficient, an element quantity from thermoelectric

measurements, from the constant, which can give rise to a more precise evaluation of the lattice thermal conductivity  $\kappa_{ph}$ .

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the support by the Austrian Science Foundation FWF under project nr. P22295-N20. The DFT calculations were done on the Vienna Scientific Cluster (VSC).

## Appendix

The relation needed in Boltzmann's transport theory is

$$K_n = \frac{1}{4\pi^3} \sum_{i,\mathbf{k}} \tau_i(\mathbf{k}) \mathbf{v}_i(\mathbf{k}) \otimes \mathbf{v}_i(\mathbf{k}) (\varepsilon_i(\mathbf{k}) - \mu)^n \left( -\frac{\partial f(\mu, T, \varepsilon_i)}{\partial \varepsilon} \right) \quad (\text{A.1})$$

in which  $\tau_i(\mathbf{k})$  is the relaxation time of the electronic states with band index  $i$ , energy eigenvalue  $\varepsilon_i$  and band velocities  $\mathbf{v}_i$  for wave vector  $\mathbf{k}$ , whereas  $f(\mu, T)$  denotes the Fermi-Dirac distribution function for the chemical potential  $\mu$  at temperature  $T$ .

The electrical conductivity  $\sigma$  is given by

$$\sigma = e^2 \mathbf{K}_0 \quad (\text{A.2})$$

and the Seebeck tensor  $\mathbf{S}$  is defined by the relation.

$$\mathbf{S} = \frac{1}{eT} \mathbf{K}_1 \mathbf{K}_0^{-1}. \quad (\text{A.3})$$

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